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(54) Title: HIGH-PRESSURE PROCESS FOR PRODUCING POLYPROPYLENE

(57) Abstract:

A process is disclosed for producing homopolymers of propylene or copolymers of propylene with other olefins or their mixtures. Polymerization is conducted under pressures from 100 to 3000 bars and at temperatures from 100 to 330°C, using a metallocene catalyst system as the catalyst.

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# HIGH-PRESSURE PROCESS FOR PRODUCING POLYPROPYLENE

## SPECIFICATION

The present invention concerns a process for producing homopolymerisates of propylene or copolymerisates of propylene with other olefins or their mixtures.

Processes for producing homo- and/or copolymerisates of propylene at low pressures and by using Ziegler catalyst systems are known, e.g., from EP-A 351 392 and EP-A 321 852. However, there are heterogeneous systems but the yields are not satisfactory and the choice of comonomers is limited.

The purpose of the present invention was thus to offer a process for producing homo- and/or copolymerisates of propylene that does not have the said shortcomings.

Accordingly, a process of homopolymerisates of propylene or copolymerisates of propylene with other olefins or their mixtures was found, in which the polymerization was done at pressure from 100 to 3000 bar and at temperatures from 100 to 330°C and a metallocene catalyst system is used as the catalyst.

Linear homopolymerisates of propylene or linear copolymerisates that have short-chain branches are obtained with this method.

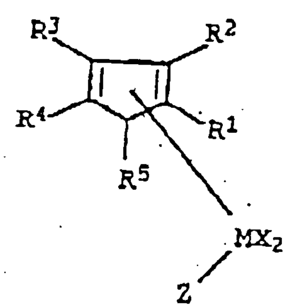
Cyclic olefins with 3-12 C-atoms, preferably 4-8 C-atoms, dienes, especially $\alpha$, $\omega$-dienes with 4-10 C-atoms such as hexadien-1,5 and olefins with 2-10 C-atoms, preferably ethylene, butene and hexene, have proven suitable as the olefins that can be polymerized with propylene, where $\alpha$-olefins are particularly preferred. These olefins can also have aryl or heteroelement substituents such as styrene or unsaturated substituted silanes.

These comonomers are usually used in amounts from 0.1 to 99.9 wt.%, preferably in amounts from 1 to 99 wt.%, relative to the amount of propylene.

Metallocene catalyst systems that contain a complex compound of metals of the IV and V subgroups of the periodic system, especially of titanium, zirconium, hafnium, vanadium, niobium or tantalum, among others, as the active constituent, are used as the catalysts. The complex compounds preferably used are those in which the metal atom is bound with unsaturated cyclic hydrocarbon atoms via $\pi$-bonds, e.g., cyclopentadienyl, fluorenyl or indenyl groups. The complex compounds preferred for use are characterized in that the metal atom can be bound with additional ligands, in particular, with fluorine, chlorine, bromine and iodine or a $C_1$-$C_{10}$-alkyl, e.g., a methyl, ethyl, propyl or butyl group. Particularly well-suited complex compounds also contain chlorine, in particular.

The preferred metallocene catalyst systems contain as the active constituents

(a) a metallocene complex of general formula I




I

in which the substituents have the following significance:

M stands for titanium, zirconium, hafnium, vanadium, niobium or tantalum,

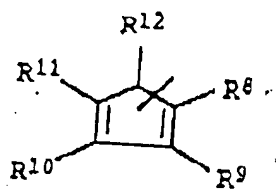
X stands for fluorine, chlorine, bromine, iodine, hydrogen, $C_1$ - $C_{10}$-

alkyl, $C_6$ - $C_{15}$-aryl or $-OR^6$,

in which case $R^6$ stands for $C_1$ - $C_{10}$-alkyl, $C_5$ - $C_{15}$-aryl, alkylaryl, arylalkyl, fluoralkyl or fluoraryl with 1-10 C-atoms in the alkyl radical and 6-20 C-atoms in the aryl radical,

$R^1$ to $R^5$ stand for hydrogen, $C_1$ - $C_{10}$-alkyl, 5- to 7-member cycloalkyl, which in turn can carry a $C_1$ - $C_6$-alkyl as substituent, $C_6$ - $C_{15}$-aryl or arylalkyl, where two adjacent radicals can also possibly stand jointly for unsaturated cyclic groups having 4-15 C-atoms, or $Si(R^7)_3$ with

$R^7$ $C_1$ - $C_{10}$-alkyl, $C_6$ - $C_{15}$-aryl or $C_3$ - $C_{10}$-cycloalkyl,

Z stands for X or 

where the radicals $R^8$ to $R^{12}$ denote hydrogen, $C_1$ - $C_{10}$-alkyl, 5-7-member cycloalkyl, which in turn can carry a $C_1$ - $C_{10}$-alkyl as substituent, $C_5$ - $C_{15}$-aryl or arylalkyl, and where two adjacent radicals can possibly also stand jointly for cyclic groups having 4-15 C-atoms, or $Si(R^{13})_3$ with

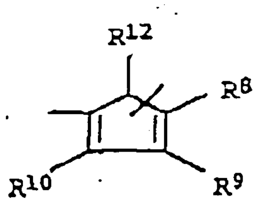
$R^{13}$ $C_1$ - $C_{10}$-alkyl, $C_6$ - $C_{15}$-aryl or $C_3$ - $C_{10}$-cycloalkyl,

or where the radicals $R^4$ and Z jointly form a $-(Y(R^{14})_2)_n$ grouping in which

Y stands for silicon, germanium, tin or carbon,

$R^{14}$ stands for $C_1$ - $C_{10}$-alkyl, $C_3$ - $C_{10}$-cycloalkyl or $C_6$ - $C_{10}$-aryl

n stands for the numbers 1, 2, 3 or 4

E stands for  or A, where A

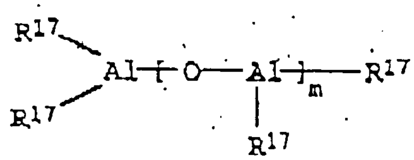
stands for —O—, —S—, $>NR^{15}$ or $>PR^{15}$

with $R^{15}$ $C_1$ - $C_{10}$-alkyl, $C_6$ - $C_{15}$-aryl, $C_3$ - $C_{10}$-cycloalkyl, alkylaryl or $Si(R^{16})_3$

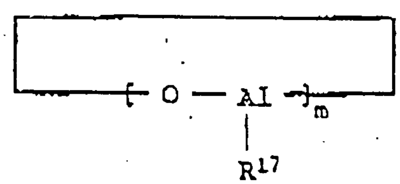
with $R^{16}$ $C_1$ - $C_{10}$-alkyl, $C_6$ - $C_{15}$-aryl, $C_3$ - $C_{10}$-cycloalkyl or alkylaryl

as well as

(b) an open-chain or cyclic alumoxane compound of general formulas II or III



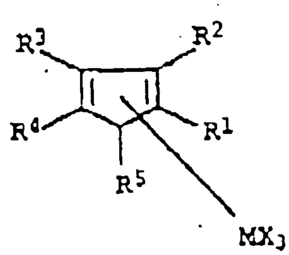
II



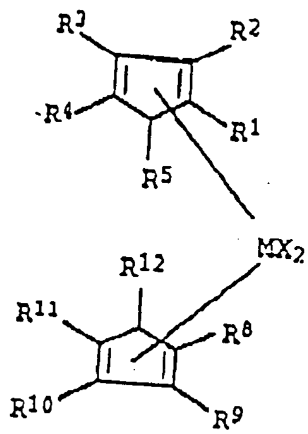
III

where $R^{17}$ signifies a $C_1$ - $C_4$-alkyl group and m stands for a whole number from 5 to 30.

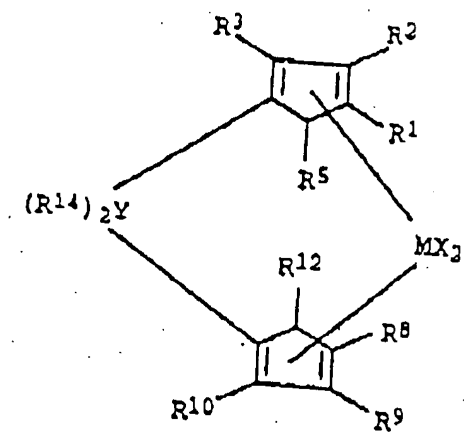
Of the metallocene complexes of general formula I, the following are preferred:



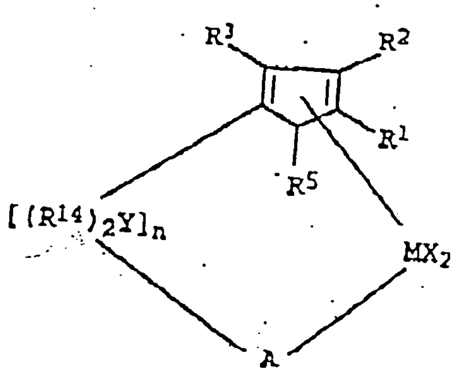
Ia,



Ib,



Ic and



Id.

Of the compounds of formula Ia, the ones particularly preferred are those in which

M signifies titanium, zirconium or hafnium,

X denotes chlorine and

$R^1$ to $R^5$ denote hydrogen or $C_1$ - $C_4$-alkyl.

Of the compounds of formula Ib, the preferred ones are those in which

M stands for zirconium or hafnium,

X stands for chlorine,

$R^1$ to $R^5$ denote hydrogen, $C_1$ - $C_4$-alkyl or $Si(R^7)_3$,

$R^5$ to $R^{10}$ denote hydrogen, $C_1$ - $C_4$-alkyl or $Si(R^{13})_3$.

The compounds of formula Ib in which the cyclopentadienyl radicals are identical are particularly well suited; unsubstituted cyclopentadienyl radicals are preferred.

Of the compounds of formula Ic, the ones particularly well suited are those in which

$R^1$ and $R^8$ are identical and stand for hydrogen or $C_1$ to $C_{10}$ alkyl groups,

$R^5$ and $R^{12}$ are identical and stand for hydrogen, a methyl, ethyl, isopropyl or tert.-butyl group

$R^2$, $R^3$, $R^9$ and $R^{10}$ have the significance

$R^3$ and $R^{10}$, $C_1$ to $C_4$-alkyl

$R^2$ and $R^9$, hydrogen, or two adjacent radicals $R^2$ and $R^3$ as well as $R^9$ and $R^{10}$ stand jointly for unsaturated cyclic groups having 4-12 C-atoms,

$R^{14}$ stands for $C_1$ - $C_8$-alkyl,

M stands for zirconium or hafnium,

Y stands for silicon, germanium, tin or carbon and

X stands for chlorine.

Examples of particularly well-suited complex compounds are, among others:

Dimethylsilandiyl bis(-3-tert.butyl-5-methyl cyclopentadienyl) zirconium dichloride,

Diethylsilandiyl bis(-3-tert.butyl-5-methylcyclopentadienyl) zirconium dichloride,

Methyl ethyl silandiyl bis(-3-tert.butyl-5-methylcyclopentadienyl) zirconium dichloride,

Dimethylsilandiyl bis(-3-tert.butyl-5-ethylcyclopentadienyl) zirconium dichloride,

Dimethylsilandiyl bis(-3-tert.butyl-5-methylcyclopentadienyl) dimethyl zirconium,

Dimethylsilandiyl bis(-2-methylindenyl) zirconium dichloride,

Diethylsilandiyl bis(-2-methylindenyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-ethylindenyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-isopropylindenyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-tert.butylindenyl) zirconium dichloride,

Diethylsilandiyl bis(-2-methylindenyl) zirconium dibromide,

Dimethylsulfide bis(-2-methylindenyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-methyl-5-methylcyclopentadienyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-methyl-5-ethylcyclopentadienyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-ethyl-5-isopropylcyclopentadienyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-methylindenyl) zirconium dichloride,

Dimethylsilandiyl bis(-2-methylbenzindenyl) zirconium dichloride and

Dimethylsilandiyl bis(-2-methylindenyl) hafnium dichloride.

Of the compounds of general formula Id, the ones that are particularly well suited are those in which

M stands for zirconium or hafnium,

X stands for chlorine or $C_1$ to $C_{10}$-alkyl,

Y stands for silicon or carbon if $n = 1$ or for carbon if $n = 2$,

$R^{14}$ stands for $C_1$ to $C_8$-alkyl, $C_5$ and $C_6$-cycloalkyl or $C_6$ to $C_{10}$-aryl,

A stands for $-O-$, $-S-$, $>NR^{15}$

and

$R^1$ to $R^3$ and $R^5$ stand for hydrogen, $C_1$ to $C_{10}$-alkyl, $C_3$ to $C_{10}$-cycloalkyl, $C_5$ to $C_{15}$-aryl or $Si(R^7)_3$.

Such complex compounds can be synthesized by known methods, where the reaction of the correspondingly substituted cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum is preferred. Examples of the corresponding production processes are described in the Journal of Organometallic Chemistry, 369 (1989), 359-370, among others.

The metallocene complexes can also be present in cationic form, as described in EP-A 277 003 and EP-A 277 004.

Besides the complex compound, the metallocene catalyst systems usually also contain oligomer alumoxane compounds of general formula II or III, where $R^{17}$ preferably stands for methyl or ethyl groups and m preferably stands for a number from 10 to 25.

These oligomer alumoxane compounds are usually produced by the reaction of a solution of trialkyl aluminum with water and is described in EP-A 284 708 and US-A 4,794,096, among others.

The oligomer alumoxane compounds obtained here are usually mixtures of both linear and cyclic chain molecules of different length, such that m can be considered a mean value. The alumoxane compounds can also be mixed with other metal alkyls, preferably with aluminum alkyls.

It has proven advantageous in the invention process to use the complex compound of metals of the IV and V subgroups of the periodic system and the oligomer alumoxane compound in amounts such that the atomic ratio between aluminum from the oligomer alumoxane compound and the transition metal from the complex compound of metals of the IV and V subgroups of the periodic system is in the range from 10:1 to $10^6$:1, especially in the range from 10:1 to $10^4$:1.

For the invention process, the catalysts are generally used in an amount from $10^{-1}$ to $10^{-9}$, preferably from $10^{-2}$ to $10^{-5}$ mols/liter of metal.

The process can be conducted in the reactors ordinarily used for high-pressure polymerization, e.g., in agitation-type autoclaves.

It has proven advantageous to mix the complex compound of metals of the IV and V subgroups of the periodic system with the oligomer alumoxane compound prior to polymerization, by which an activated catalyst system is formed. The duration of this activation step is usually 1-120 minutes, preferably 10-100 minutes. The mixing is preferably carried out so that the complex compound is brought in contact with a solution of the oligomer alumoxane compound in an inert solvent, e.g., in benzene, toluene, hexane, heptane or their mixtures, at temperatures from 0 to 50°C.

The invention process can be conducted so that the solutions of complex compounds and oligomer alumoxane compounds are mixed before the reactor and/or fed into the reactor at several sites. The polymerization can be conducted batchwise or continuously. The process is conducted at pressures of 100 to 3500 bar, preferably from 1000 to 3000 bar and at temperatures from 100 to 330°C, preferably from 120

to 300°C, especially from 120 to 250°C. The residence times are in the range from 20 to 240, preferably from 30 to 120 seconds.

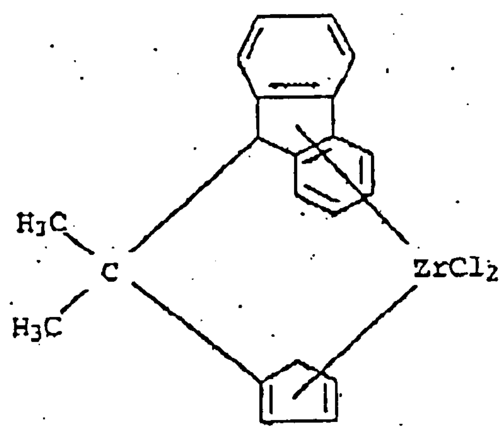
The essential advantages of the invention process are that high productivities are obtained, that the selection of comonomers is very great and that high conversions are obtained with short residence times and high molecular weights.

EXAMPLES

EXAMPLE 1

Production of a propylene homopolymerisate (PP)

440 mg ( = 1 mmol) of




Ic'

was dissolved in a mixture of 50 ml (36 g, 0.5 mol) of aluminum trimethyl and 290 g of 1.53 molar toluene methyl aluminoxane solution (0.5 mol) in 10 l of toluene. Excluding air and moisture, 10 $m^3$ of propylene/h and the above-described solution were metered into a continuously operating high-pressure agitation autoclave.

Table 1 gives the experimental conditions and the results.

The mean molecular weight $\overline{M}_w$ (mean weight value) was determined by gel permeation chromatography.

TABLE 1:

| Temperature (°C) | Pressure (bar) | g Ic'/h | Residence time (min) | Productivity (g PP/g Ic'.h) | $\overline{M}_w$ |
|---|---|---|---|---|---|
| 149 | 1510 | 0.17 | 1.5 | 8380 | 2000 |

EXAMPLE 2

Production of a propylene-ethylene copolymerisate

The procedure was as in Example 1, but a mixture of propylene and ethylene was polymerized.

The experimental conditions and the results are given in Table 2.

TABLE 2:

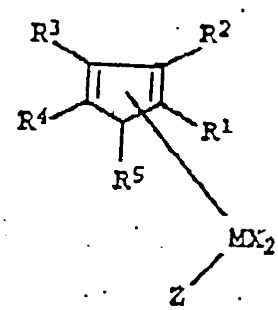
| Temperature (°C) | Pressure (bar) | g Ic'/h | wt.% of propylene to wt.% of ethylene in the gas mixture | Productivity (g of polymer/g of Ic'/h) | $\overline{M}_w$ |
|---|---|---|---|---|---|
| 190 | 1508 | 0.078 | 24 358 | 24 358 | 10,000 |

PATENT CLAIMS

1. Process for the production of homopolymerisates of propylene or copolymerisates of propylene with other olefins or their mixtures, characterized in that the polymerization is conducted at pressures of 100 to 3000 bar and at temperatures from 100 to 330°C and a metallocene catalyst system is used as the catalyst.

2. Process according to claim 1, characterized in that a metallocene catalyst system contains the following as active constituents:

(a) a metallocene complex of general formula I



I

in which the substituents have the following significance:

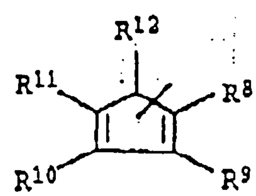
M stands for titanium, zirconium, hafnium, vanadium, niobium or tantalum,

X stands for fluorine, chlorine, bromine, iodine, hydrogen, $C_1$ to $C_{10}$-alkyl, $C_6$ to $C_{15}$-aryl or $-OR^6$,

where $R^6$ denotes $C_1$ to $C_{10}$-alkyl, $C_6$ to $C_{15}$-aryl, alkylaryl, arylalkyl, fluoralkyl or fluoraryl with 1-10 C-atoms in the alkyl radical and 6 to 20 C-atoms in the aryl radical,

$R^1$ to $R^5$ stand for hydrogen, $C_1$ to $C_{10}$-alkyl, 5- to 7-member cycloalkyl, that in turn can carry a $C_1$ to $C_{10}$-alkyl as substituent, $C_6$- to $C_{15}$-aryl or arylalkyl, where two adjacent radicals can possibly also stand jointly for cyclic groups having 4-15 C-atoms, or $Si(R^7)_3$ with

$R^7$ $C_1$- to $C_{10}$-alkyl, $C_6$- to $C_{15}$-aryl or $C_3$- to $C_{10}$-cycloalkyl,

Z stands for X or 

where the radicals $R^8$ to $R^{12}$ denote hydrogen, $C_1$- to $C_{10}$-alkyl, 5- to 7-member cycloalkyl, which in turn can carry a $C_1$- to $C_{10}$-alkyl as substituent, $C_6$- to $C_{15}$-aryl or arylalkyl, and where two adjacent radicals can possibly also stand jointly for cyclic

groups having 4-15 C-atoms, or $Si(R^{13})_3$ with

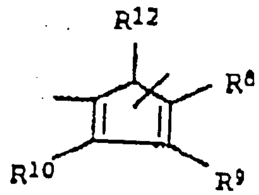
$R^{13}$ $C_1$- to $C_{10}$-alkyl, $C_6$- to $C_{15}$-aryl or $C_3$- to $C_{10}$-cycloalkyl,

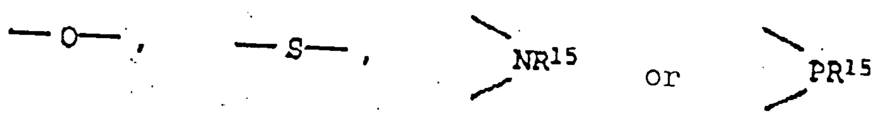
or where the radicals $R^4$ and Z jointly form a grouping $-(Y(R^{14})_2)_n-E-$, in which

Y stands for silicon, germanium, tin or carbon,

$R^{14}$ stands for $C_1$- to $C_{10}$-alkyl, $C_3$- to $C_{10}$-cycloalkyl or $C_6$- to $C_{15}$-aryl,

n stands for the numbers 1, 2, 3 or 4,

E stands for  or A, where A signifies

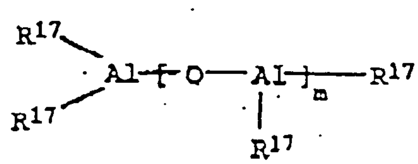




with $R^{15}$ $C_1$- to $C_{10}$-alkyl, $C_5$- to $C_{15}$-aryl, $C_3$- to $C_{10}$-cycloalkyl, alkylaryl or $Si(R^{16})_3$

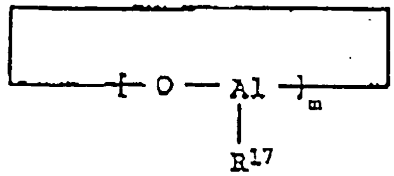
with $R^{16}$ $C_1$- to $C_{10}$-alkyl, $C_6$- to $C_{15}$-aryl, $C_3$- to $C_{10}$-cycloalkyl or alkylaryl

as well as

(b) an open-chain or cyclic alumoxane compound of general formula II or III




II



III

where $R^{17}$ signifies a $C_1$- to $C_4$-alkyl group and m stands for a whole number from 5 to 30.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 92/02017

**A. CLASSIFICATION OF SUBJECT MATTER**

Int.Cl.5 C08F 10/06, C08F 4/602

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | DE, A, 3150270 (EC ERDÖLCHEMIE) 30 June 1983, see claims; page 3, lines 23-28 | 1,2 |
| X | WO, A, 9104257 (EXXON) 4 April 1991 see claims; page 22, lines 9-29; example 55 | 1,2 |
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☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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